

## REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-03-

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 13 NOV 03	3. REPORT TYPE FINAL REPORT	1 JUN 01 TO 31 MAY 03
4. TITLE AND SUBTITLE PHOTOELECTRON SPECTROMETER AND CLUSTER SOURCE FOR THE PRODUCTION AND ANALYSIS OF CLUSTER ASSEMBLED NANOSCALE MATERIALS		5. FUNDING NUMBERS F49620-01-1-0380 3484/FS 61103D	
6. AUTHOR(S) A.W. CASTLEMAN, JR.		8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) PENNSYLVANIA STATE UNIVERSITY CHEMISTRY AND PHYSICS DEPARTMENT UNIVERSITY PARK, PA 16802		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 4015 WILSON BLVD, ROOM 713 ARLINGTON, VA 22203-1954		11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION AVAILABILITY STATEMENT APPROVE FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The overall objective of our presently funded AFOSR program is to lay the scientific foundation for designing strategies to be employed for the formation of cluster assembled materials (CAMs) of nanoscale dimensions that possess selected properties. Studies thus far have yielded information on reactivity and are providing insight on methods of producing building blocks having the desired stoichiometry, size, and properties. Findings from studies of relaxation dynamics are yielding insights into electronic characteristics which influence the properties of CAMs that may function as catalysts, or alternatively find application as new optical and electronic materials, or ones potentially useful as sensors.			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT		18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT
			20. LIMITATION OF ABSTRACT

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## **AFOSR FINAL (DURINT) REPORT**

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### **Research Title:**

Photoelectron Spectrometer and Cluster Source for the  
Production and Analysis of Cluster Assembled Nanoscale  
Materials

### **Grant No:**

F49620-01-1-0380

**DISTRIBUTION STATEMENT A**  
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Distribution Unlimited

### **Period of Performance:**

June 1, 2001 – May 31, 2003

## **Introduction**

We are engaged in a continuing basic research program in this field entitled "Cluster Dynamics: Foundations for Developing Nanoscale Materials", supported through the AFOSR. As indicated by the title of the grant, this fundamental research activity has the goal of providing the underpinning knowledge for undertaking a unique approach unlike that being pursued by most other research groups, namely forming new materials of nanoscale dimensions using clusters as building blocks – an approach "from the bottom up," rather than from the more conventional "top down method" which typically involves the subdivision of matter of bulk dimensions. Hence the goal is to achieve the ability to produce nanoscale materials of tailored properties.

The overall objective of our presently funded AFOSR program is to lay the scientific foundation for designing strategies to be employed for the formation of cluster assembled materials (CAMs) of nanoscale dimensions that possess selected properties. Studies thus far have yielded information on reactivity and are providing insight on methods of producing building blocks having the desired stoichiometry, size, and properties. Findings from studies of relaxation dynamics are yielding insights into electronic characteristics which influence the properties of CAMs that may function as catalysts, or alternatively find application as new optical and electronic materials, or ones potentially useful as sensors.

Systems of finite size often display unique properties, differing from those of either the extended solids or of the individual molecular constituents of which the solids are comprised. This typically arises due to the fact that their properties are determined by quantum effects where size constraints directly influence energy levels and, hence in turn, the reactive nature of the systems. Particularly interesting in this context are cluster systems whose size and composition can be selectively chosen, and ones whose individual characteristics can be retained, thus allowing them to serve as the building blocks for cluster assembled materials (CAMs). The prospects that collective effects can be displayed by materials of nanoscale dimension opens the avenue for exploring the use of clusters of specific stoichiometry and oxidation, or even charge state, as the building

blocks. There is a rapidly increasing interest in the field of nano-science and technology in the context of these considerations, too.

The present program is directed to 1) developing approaches for synthesizing cluster assembled nanoscale materials of unique properties, with particular attention to elucidating their reactive behavior, dynamics of formation, and electronic properties; 2) exploring methods for storing highly energetic materials through cluster stabilization; and 3) establishing concepts for tailoring the design of nanoscale catalysts that may find application in the area of energetic materials. One major thrust of the current work is devoted to a study of Met-Cars, a unique class of transition metal carbon clusters discovered in our laboratory, while another is focused on energetic materials comprised of aluminum alloys, where these species have been identified as being highly reactive in particular cluster sizes, but also exhibiting the potential for being stabilized through cluster assembly concepts.

The work builds heavily on a femtosecond laser system acquired through a DURIP grant, with the scope of our program now expanded due to the availability of a high intensity cluster source and photoelectron spectrometer made possible through a DURINT grant. Specifically, the new equipment enables us to explore the concepts of cluster assembly through ascertaining the evolving electronic band structures of the materials of varying sizes and compositions, providing underlying fundamental concepts for producing nanoscale materials. An overview and details of the new equipment are provided in what follows.

### **Photoelectron Spectrometer and Cluster Source Acquired Through DURINT Funding:**

#### **Overview**

The new equipment is intended to compliment our existing facility where research interests are rooted in further developing strategies that can be implemented for tailor designing materials with desired properties. In terms of AFOSR interests, effort now will be devoted to devising methods of forming the building blocks of new materials that may exhibit unique wear resistance, strength, and hardness on the one hand, or that display unusual catalytic or reactive behavior on the other. Consideration will also be given to

the formation of materials of unique electronic nature for possible use as quantum dots or perhaps as sensors, and also exploring the possibility of producing new materials comprised of reactive metal atoms that can be stored in a stable state, yet readily utilized as an additive to fuels to greatly increase their energy content. Research is underway to elucidate the properties of potential materials that may be employed as new structural and electronic materials, as well as catalysts and also energy storage devices.

The main properties under consideration in our work involve knowledge of the electronic states of clusters and related nanoscale aggregates. In this context we intend to expand the scope of our studies made possible through the new acquisition of funding to construct and implement a photoelectron spectrometer and new intense cluster source. The availability of this equipment has opened up a number of avenues in the exploration of new concepts of forming cluster assembled nanoscale materials. Besides the seamless extension toward applying the laser pump-probe technique to the larger species, the new source provides ample material for investigations employing the photoelectron spectrometer. The photoelectron kinetic energy analyzer is central to studies of the electronic relaxation dynamics, providing information about the electron affinities and hence the band structures of the cluster assemblies as they are developed from various building blocks. The insight gained with this technique is crucial in assessing the changes in properties, which are expected to be affected through the selected assembly of cluster building blocks. The use of the photoelectron spectrometer will not only enhance our current understanding of these systems but is necessary to obtain a quantitative understanding of the electronic properties inherent to specific materials.

#### **Photoelectron Spectrometer and Cluster Source (Durint Grant)**

Previously, we utilized a reflectron time-of-flight mass apparatus that was coupled to a laser vaporization cluster source. While the cluster source was efficient for the study of neutral cluster dynamics, we were limited in our ability to produce large clusters. This limitation, although a common one when utilizing a laser vaporization source, must be resolved to perform photodetachment experiments. This is a direct result of the small photodetachment cross-sections one encounters when studying anions. We have designed a new source that produces larger cluster species in larger quantities. The

details regarding our improved cluster source and anion photoelectron facility are described herein.

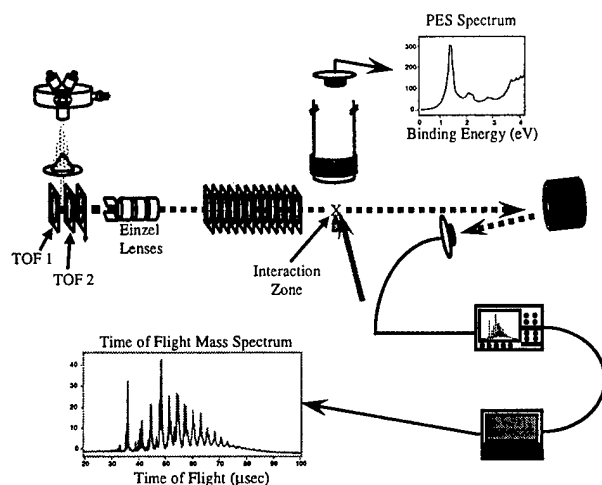


Figure 1. Schematic representation of newly constructed anion cluster photoelectron apparatus.

The construction phase of a photoelectron spectrometer and laser vaporization cluster source is completed. The newly assembled apparatus is represented schematically in Figure 1. The finished facility is depicted in Figures 2 and 3 (on next page). In addition to being able to

determine the electronic properties of various cluster assembled materials, our new source provides us with the ability to produce a wide range of cluster materials. The addition of ion optics allowing mass selection provides the opportunity to determine the influence of sequential cluster size, by enabling the direct characterization of a specific species in an isolated environment.

We have designed and constructed a new source, into which we have incorporated dual pulsed valves. Anions, having high internal energy, are difficult to cool efficiently. The additional pulsed valve overcomes this problem by creating a more intense supersonic expansion, which

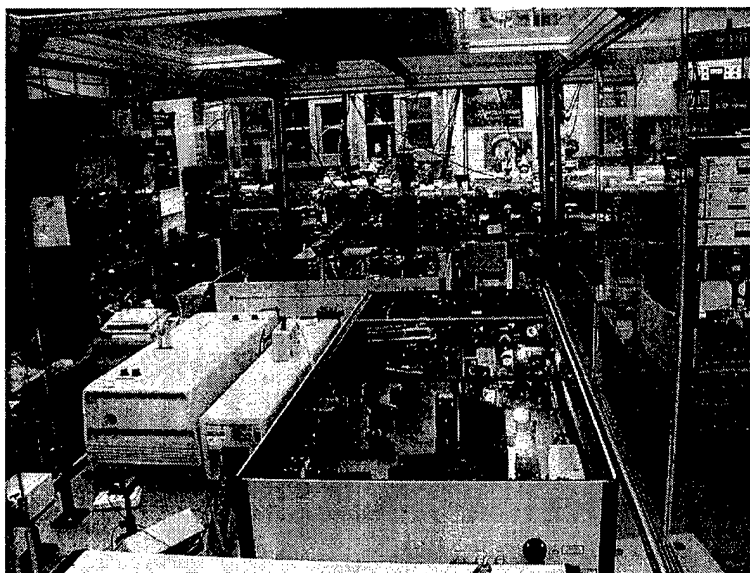


Figure 2. Ti:sapphire femtosecond laser system purchased through DURIP grant.

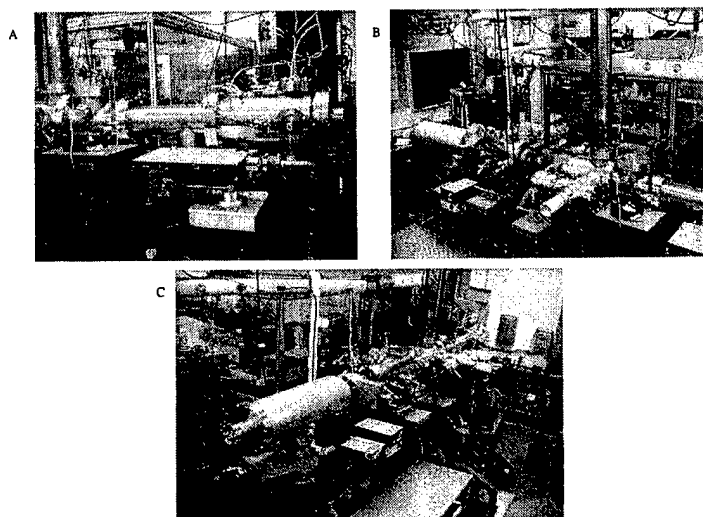


Figure 3. Picture of: a) newly constructed source region, b) magnetic bottle photoelectron spectrometer, and c) view of anion mass spectrometer and PES.

better cools the molecular packet, ultimately resulting in increased cluster aggregation, and subsequently stabilizes larger cluster species. More importantly, in addition to producing larger clusters, the species are produced in greater abundance.

The implementation of an additional pulsed valve increases the amount of gas in

the source region of our mass spectrometer. We have added additional diffusion and turbomolecular pumps to help evacuate the large gas volume created by our new source. We have also studied the effect of varying the size of the inlet aperture to the extraction region.

The anion cluster distribution is characterized by a Wiley-McLaren type time-of-flight mass spectrometer. Mass analysis allows us to monitor the cluster distribution while source conditions are optimized to enhance the species we wish to study. The source has been used to prepare anion distributions of vanadium oxide clusters, Met-Cars, copper oxides, hydrocarbons and oxygen. The versatility of the laser vaporization source to produce anion distributions is evident in Figure 4, where different species are recorded.

Many measures have been taken to enhance the resolution of the anion mass spectrometer as well as to calibrate the data obtained from it. First, great care was taken

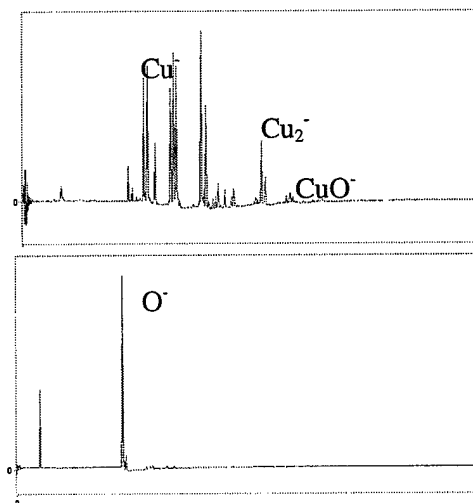


Figure 4. Anion distribution of CuO- clusters (top) and O- (bottom)

in developing the most appropriate electronic circuitry for acquiring the appropriate amplified signals from the multichannel plate detectors employed to measure the anion and electron arrival spectra. Advanced circuitry was found to be desirable to minimize the effects of ringing on the resolution. Other measures to enhance resolution included the introduction of extraction grids with mesh of varying sizes to obtain mass peaks with the sharpest temporal resolution. We have also adjusted the extraction potentials to manipulate the space-focusing to create a distribution with the desired properties. Emphasis has been placed on the effect various ion optics would have on the extraction region. We have explored these components through both experimentation and computer simulations. One such ion optic is the Einzel lens, which creates a cylindrical electrostatic field that focuses the ion packet by the nature of its symmetrical field gradient. Ion deflectors have also served as a useful addition to compensate for ions directed off axis relative to the detector.

As has been mentioned previously, the ability to mass select a specific species from the distribution provides us with a unique opportunity to obtain direct information regarding the effect cluster formation has on electronic properties. In practice, this is achieved by disrupting the trajectory of ionic species with an electrostatic potential with enough intensity to alter their path. The potential is then removed to allow the desired species to pass. The limiting factor, which ultimately needs to be overcome, is the ability to remove and reapply this blocking field quickly enough, typically on the order of microseconds. This was accomplished in our laboratory with fast electronic switches. The

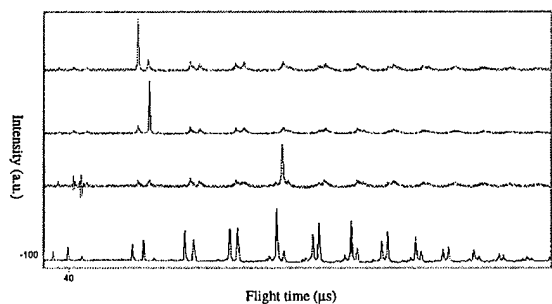


Figure 5. Mass distribution of  $V_m O_n^-$  clusters.

Figures a-c demonstrate the ability of mass selection: a)  $V_2O_3^-$ ; b)  $V_2O_4^-$  and c)  $V_5O_{10}^-$ . The entire distribution is shown in 3d.

switch is provided with a starting pulse or “trigger” at which time it closes a circuit effectively removing the blocking field described above. This starting pulse is given a width, at the end of the pulse the blocking field is restored. As our source may provide mass species with separation as little as sub-microseconds, it is necessary to employ and remove these



fields on comparable time scales. We have been able to mass select with great efficiency as shown in Figure 5 (above).

Following the mass gate, we have included an ion deceleration assembly. The deceleration assembly is pulsed in a manner analogous to the mass gate. However, the species of interest is subjected to the electrostatic gradient. This assembly provides a uniform deceleration field, which compensates for any differences in the energy distribution of the ion packet resulting from extraction. The decelerator is essential for high resolution when conducting photodetachment experiments. The energy spread of the mass selected ion packet is as follows:  $\Delta E_f = (E_f/E_i)^{1/2} \Delta E_i$ , where  $E_f$  is the final energy of the species at the point of detachment. The decelerator greatly decreases this value, thereby improving resolution. The effect of deceleration on the ion packet is demonstrated in simulation presented in Figure 6.

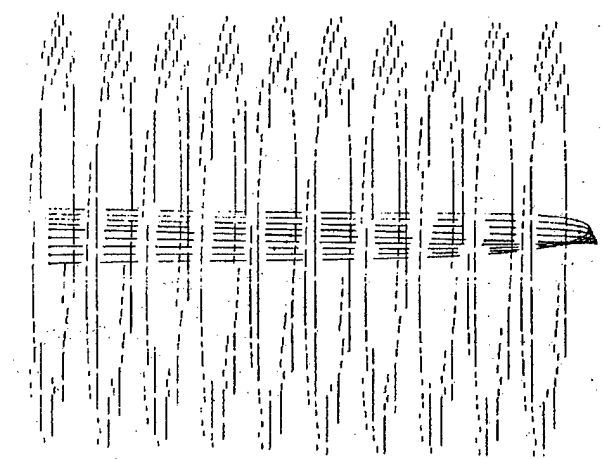


Figure 6. Simulations of deceleration assembly showing ability to decrease velocity as well as focus the packet.

Our ultrafast laser system is tunable over a broad range of photon energies. The photon wavelength most suitable for the species being studied is selected, and the laser beam is then intersected with the anion resulting in the photodetachment of electrons. Upon detachment, electrons feel a very strong (1Tesla) magnetic field generated by the aforementioned permanent magnet.

The electrons are then pushed away from the strong field toward our electron detector. The permanent magnet was machined to have a conical shape. This geometric alteration causes the field to become highly divergent. Since electrons move away from strong magnetic fields, this divergence helps to corral the electrons. Next, the electrons enter a drift tube similar to that of the drift tube of the anion mass spectrometer. The drift tube is a high vacuum area, which is comprised of a solenoid that generates a uniform magnetic field of low strength (1 mT). The low field in the drift region compensates for the earth's magnetic field, and directs electrons to the detector. A solenoid generates a magnetic field when current flows through a

helical path. We have created a solenoid by wrapping our electron flight tube with copper wire and passing current through it to generate the desired magnetic field. We have also taken the preventative measure of wrapping the electron flight tube with carefully chosen cylinders of mu-metal. The mu-metal shields our photoelectron spectrometer from any stray magnetic fields that may be generated by external sources, such as electronic components, motors and so forth, without it the electrons may be deflected off axis and not reach the detector.

We have constructed a translation stage to which a permanent magnet is mounted. This translation provides the ability to control the position of the magnet in three dimensions. This enables us to manipulate the magnet to a position that will provide the most significant enhancement to the photoelectron signal. We have constructed a mount from non-magnetic stainless steel, which supports the magnet and ensures that it is electronically grounded.

As mentioned above, an important addition to our detection scheme was made to facilitate the detection of negatively charged particles (both anions and electrons). Since our detector is used for both positively and negatively charged particles, a new capacitive coupled fast transimpedance amplifier was constructed. For positively charged particle detection, a high voltage is applied to the cathode side of the detector, and the anode (collector) electronically floats (no potential is applied). If electrons or anions are to be detected, the high voltage is applied to the anode part, which creates a circuitry problem. If a short, high voltage burst were to pass through the coupling capacitor, the electronics directly connected to the capacitor could be damaged. We worked closely with the Research Instruments Electronics Support staff on our site to develop two fast transimpedance amplifiers for our detection- one for anions and the other for electrons. Our new detection electronics are designed to have a high input impedance and low output impedance, and are easily incorporated into an already-existing combination of microchannel plate detection and oscilloscope output.

We have confirmed the photoelectron spectrometer is operational by ablating stationary targets. The photoelectrons ejected from these targets are collected with high efficiency. Figure 7 (below) depicts time-resolved electron signal.

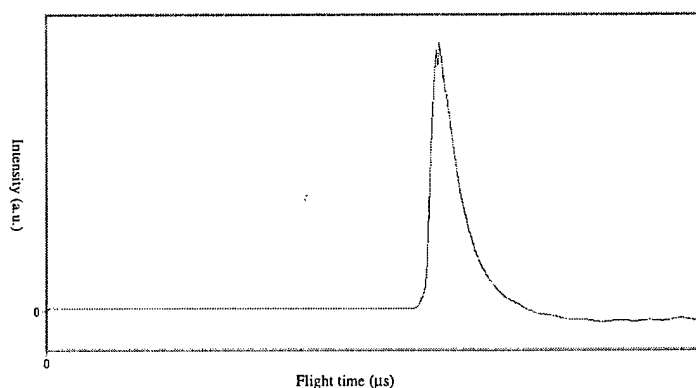


Figure 7. Time resolved electron signal.

The proceeding describes measures we have taken to construct an apparatus capable of producing reliable photoelectron data, and we have proceeded in a manner that provides the most versatile instrument. The

anion time-of-flight mass spectrometer described thus far operates in a linear mode. This mode of operation is most useful for monitoring effects electrostatic and magnetic fields may have on the ion packets trajectory. The linear mode is also preferential for determining the most appropriate mass selection conditions. We also have constructed the instrument in such a manner that it may operate in a reflectron mode. In this way, an additional ion optic, the reflectron, can be employed to increase the resolution of the observed ion distribution. Our group has reported pioneering studies by extending the use of reflectron mass spectrometers to unravel the mechanisms of photodissociation processes. This mode of operation will also be valuable when employed to study the stability and reactivity of various cluster systems.

Finally, an extensive electronic safety system has been developed for monitoring the internal conditions of our newly constructed instrument. Various pressure, thermal and water gauges have been interlocked with a feedback unit that will alert operators to any undesirable conditions, and if necessary have been programmed to disable any necessary component to eliminate the possibility of damage.

Each component has been successfully constructed and is in working order; conducting novel research on interesting cluster systems seemingly should be straightforward. As was mentioned previously, we have demonstrated the ability to produce various metal oxides and as such intend to study these systems in great detail. Certainly as research proceeds, optimizations will be made to improve the capabilities of our instrument in any way feasible or necessary. We intend to move our newly

constructed source to the vacuum region. It is our belief that this will enhance its efficiency and make it less vulnerable to damage.

A major focus of the ongoing program deals with the dynamics of cluster formation, growth, and reactivity of Met-Cars, a unique class of transition-metal-carbon clusters of  $M_8C_{12}$  composition, discovered in our laboratory. Another objective is to develop methods of stabilizing aluminum cluster compounds of potential value in energy storage. We plan to extend our investigations to other cluster systems that represent promising building blocks for CAMs, including a study of the properties of these nanoscale composites deposited on surfaces.

**Personnel Supported:**

A. W. Castleman, Jr., Principal Investigator  
Ken Knappenberger, Ph.D. Student  
Brian Leskiw, Ph.D. Student  
Margaret Lyn, Ph.D. Student  
Eric Wisniewski, Ph.D. Student

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**Interactions/Transitions:** *Participation/presentations at meetings, conferences, seminars, etc.:*

- "The Science of Small (Nano) Particles and Clusters: Evolution of the Field, High Lights Prospects for the Future", ISSPIC 11 Meeting, Strasbourg, France, September 9-13, 2002.
- "Reactions of Transition Metal Oxide Clusters: Insights into Mechanisms of Catalytic Reactions," (invited talk), Philip Morris Incorporated, Richmond, VA, October 14, 2002.
- "Clusters: Insights into Surface Reactions and Catalysts", (invited talk), 1<sup>st</sup> University of California Symposium on Surface Science and its Applications, UC Riverside, CA, February 13-14, 2003.

- “Update on Met-Cars: Production, structure, and spectroscopy,” (talk Lisa Lyn), 225<sup>th</sup> ACS National Meeting, New Orleans, LA, March 23-27, 2003.
- “Clusters: Building Blocks of Nanoscale Materials,” University of Pittsburgh Department of Chemistry Seminar, Pittsburgh, PA, April 3, 2003.
- “Clusters: Insights In Surface Reactions and Catalysis,” Frontiers Lecture, Wayne State University, Detroit, MI, April 7, 2003.
- “Nanoscale Matters,” Albany International Distinguished Lecture in Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY, April 17, 2003.
- “Clusters: Insights into Surface Reactions and Catalysis,” Physical Chemistry Seminar, Ohio State University, Columbus, OH, May 5, 2003.
- “Met-Cars: Mass Deposition and Preliminary Structural Study via TEM,” (talk Jenny Gao), ICIM 2003 (Fifth International Conference on Intelligent Materials) State College, PA, June 14-17, 2003.
- “Developments in Molecular Electronics and Nanoscale Science,” (Overview and Session Introduction) International Symposium – Joshua Jortner’s Honor, Tel Aviv, Israel, June 16-18, 2003.
- “Dynamics of Cluster Ionization Processes,” SFB Colloquium/Physic Department, Freie Universitatet Berlin, June 24, 2003.
- Introducer and Discussion Leader, Femtochemistry VI, Paris, France, July 6-10, 2003.
- “Dynamics of Systems of Restricted Size: Influence of the Degree of Aggregation,” ISACC 2003, St. Petersburg, Russia, July 18-21, 2003.
- “Cluster Reactions: Laying the Foundations for Cluster Assembled Materials,” Gordon Research Conference, New London, CT, August 3-8, 2003.
- “Clusters: Concepts for Developing Nanoscale Catalysts,” Symposium “Materials Design Using Molecular Simulation,” Cancun, Mexico, August 17 – 21, 2003.

“Clusters: Insights into Surface Reactions and Catalyst Involving Oxygen Transfer Processes,” Symposium on Chemistry on Size Selected Metal Clusters, ACS Meeting, New York, NY, September 7-11, 2003.

“Cluster Dynamics: Laying the Foundation for Cluster Assembled Materials”, SUNY Stony Brook, Stony Brook, NY, October 16-17, 2003

“Advances in Cluster Research,” FELIX Group Seminar, FOM-Institute for Plasma Physics, Amsterdam, The Netherlands, Oct. 20, 2003.

“Clusters: Building Blocks of New Materials,” International Congress on Materials Science and Nanotechnology NANOMAT- 2003, Brussels, Belgium, October 22-24, 2003.

Chairman of Session F: Advanced Materials I: Novel Technologies and Methods, International Congress on Materials Science and Nanotechnology NANOMAT- 2003, Brussels, Belgium, October 22-24, 2003.